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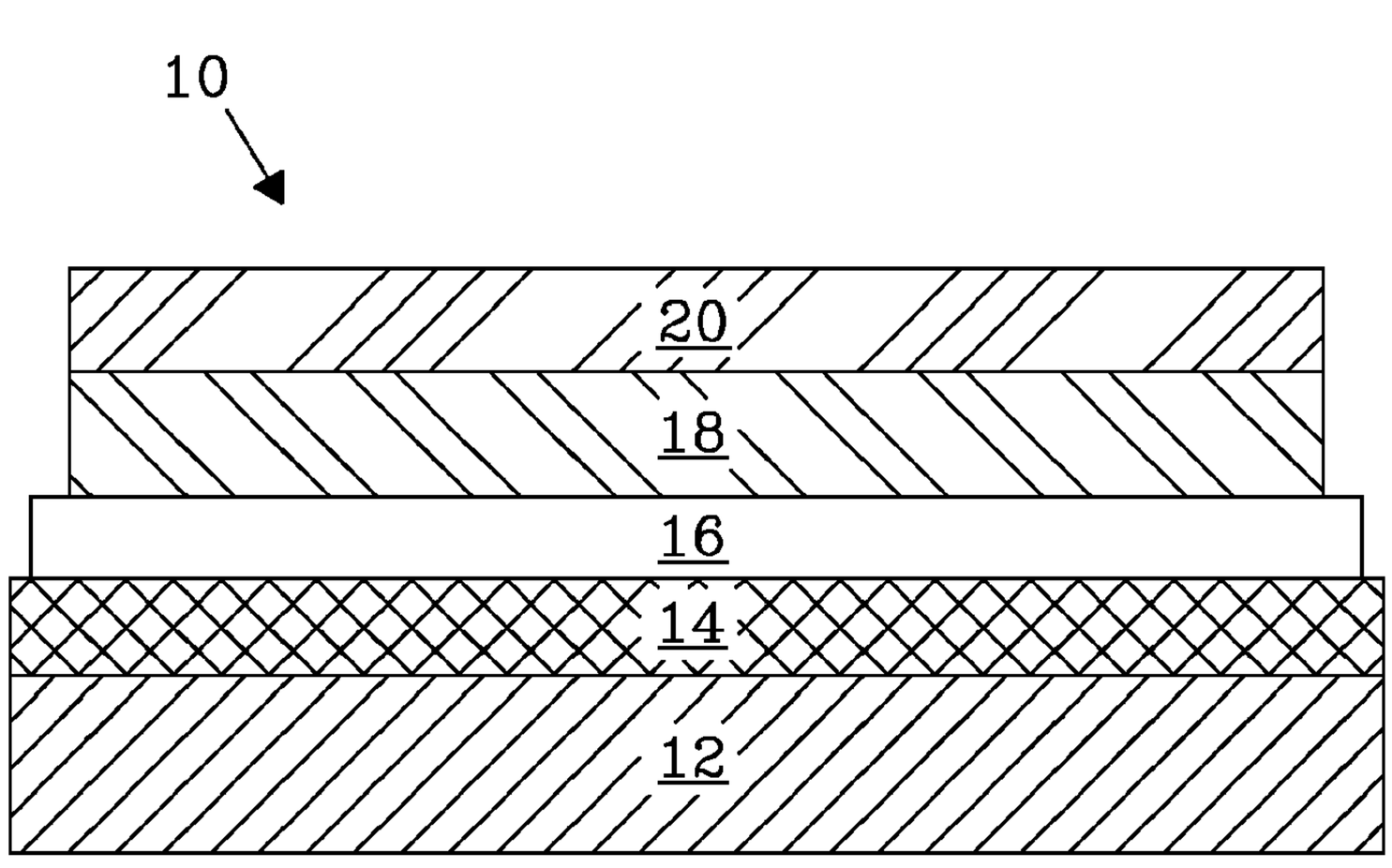
(54) **Titre : CONFIGURATIONS CELLULAIRES OPTIMISEES POUR DES PILES A COMBUSTIBLE A OXYDE SOLIDE A BASE DE LSCF STABLE**
(54) **Title: OPTIMIZED CELL CONFIGURATIONS FOR STABLE LSCF-BASED SOLID OXIDE FUEL CELLS**



(57) **Abrégé/Abstract:**
Lanthanum strontium cobalt iron oxides (La(1-x)SrxCoyFe1-yO3-f; (LSCF) have excellent power density (> 500 mW/cm2 at 750°C). When covered with a metallization layer, LSCF cathodes have demonstrated increased durability and stability. Other modifications, such as the thickening of the cathode, the preparation of the device by utilizing a firing temperature in a designated range, and the use of a pore former paste having designated characteristics and combinations of these features provide a device with enhanced capabilities.

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(54) Title: OPTIMIZED CELL CONFIGURATIONS FOR STABLE LSCF-BASED SOLID OXIDE FUEL CELLS

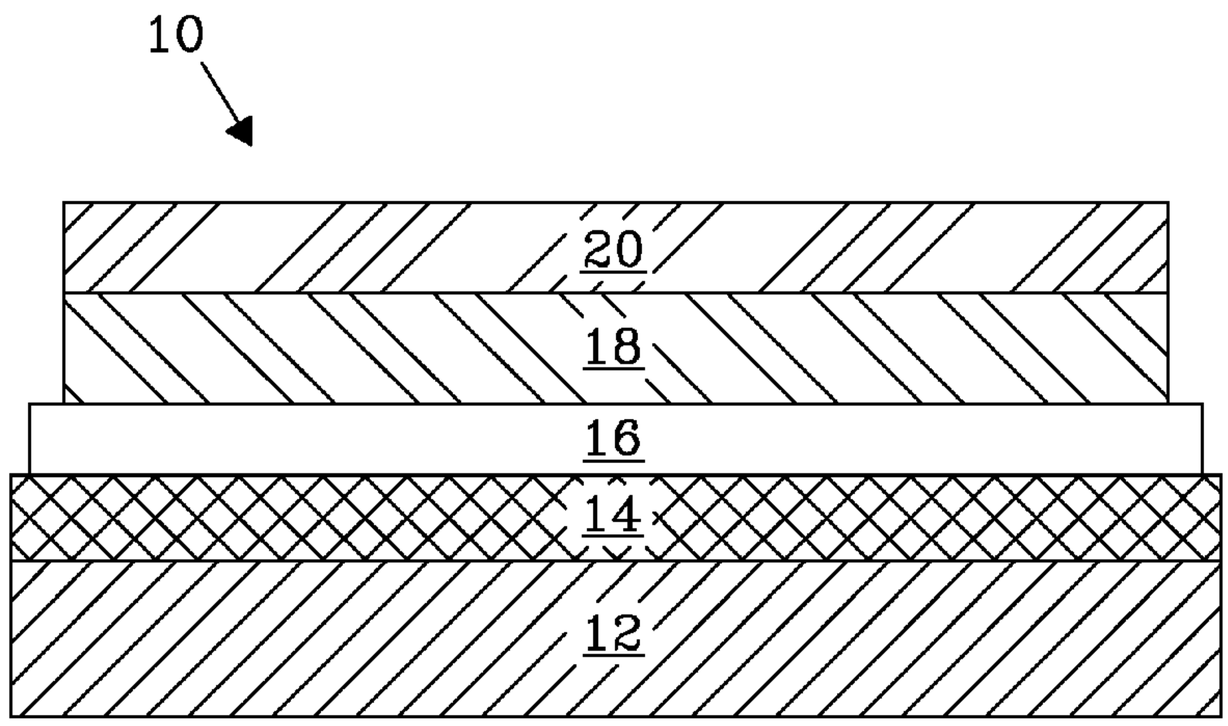

Fig. 1

(57) Abstract: Lanthanum strontium cobalt iron oxides (La(1-x)SrxCoyFe1-yO3-*f*; (LSCF) have excellent power density (>500 mW/cm2 at 750°C). When covered with a metallization layer, LSCF cathodes have demonstrated increased durability and stability. Other modifications, such as the thickening of the cathode, the preparation of the device by utilizing a firing temperature in a designated range, and the use of a pore former paste having designated characteristics and combinations of these features provide a device with enhanced capabilities.

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OPTIMIZED CELL CONFIGURATIONS FOR STABLE LSCF-BASED SOLID OXIDE FUEL CELLS

Background of the Invention

[0001] Lanthanum strontium cobalt iron oxides (La(1-x)SrxCoyFe1-yO3-*f*Ô; LSCF) have excellent power density (>500 mW/cm2 at 750 °C). However, the use of these materials in solid oxide fuel cell (SOFC) applications has been hindered because of various problems associated with the degradation in power with time. What is needed therefore is a cell configuration that enables the use of these materials while minimizing the degradation typically associated with the use of such materials. Illustrative embodiments of the present disclosure may meet these needs.

[0002] Additional advantages and novel features of illustrative embodiments will be set forth as follows and will be readily apparent from the descriptions and demonstrations set forth herein. Accordingly, the embodiments described below should be seen as illustrative of the invention and not as limiting in any way.

Summary

[0003] An illustrative embodiment of the present invention is a cathode made from a high power SOFC cathode materials possessing thermal expansion mismatch with a adjacent material. Lanthanum strontium cobalt iron oxides (La(1-x)SrxCoyFe1-yO3-$f\hat{O}$; LSCF) have excellent power density (>500 mW/cm2 at 750 °C). The biggest problem associated with use of these materials for SOFC applications is the degradation in power with time. We found that the degradation rate of the LSCF cathode is closely related to the cell configuration and metallization as well as firing conditions, which influences the electrical conductivity and oxygen supply to the cathode.

[0004] This degradation problem can be remedied by the placement of a fully covered metallization layer on a lanthanum strontium cobalt iron oxide cathode layer within the SOFC. This metallization layer is preferably made from a noble metal and their alloys. In particular embodiments, those containing silver and silver alloys such as silver-palladium have been deemed effective. Other materials, including ceramics such perovskites (similar to cathode materials), can also be utilized. Thickening of the cathode, the preparation of the device by utilizing a firing temperature in a designated range and the use of a pore former paste having designated characteristics and combinations of these features provide a device with enhanced capabilities.

[0005] In one embodiment, a cathode for use in a solid oxide fuel cell has a metallization layer covering more than 90 percent of the cathode. In some embodiments this cathode includes at least one lanthanum strontium cobalt iron oxide. This cathode may have a porosity of between 0-30 volume percent, thickness ranging from between 2 ~ 80 μm or both. Preferably the metallization layer has a thickness of between 10 and 25 percent of the thickness of the cathode. The cathode may be formed by heating a paste at a temperature between 950 ~ 1100 °C. This paste may have a pore former having 0~30 vol% with respect to the volume of LSCF in the cathode forming paste.

[0006] In some embodiments of the invention, various microcracks are created in the cathode. These microcracks are typically formed during the heating process (firing) and can be influenced by a variety of factors. These include the thickness of cathode (the thicker, the more cracks), the firing temperature (the higher, the more in the range described in the patent), the pore former (the less, the more), the character of the cathode paste (the finer, the less), the tap density of powder (the higher, the more), etc.

[0007] Full coverage of a metallization layer assists to ensure the current collection of the cathode with microcracks. However in some embodiments, overall full coverage has shown a better stability even without microcracks. Cathode porosity is continuous pores throughout the

cathode layer. It is interconnected in a fine scale. The microcracks refer to discontinuity in the cathode layer. The cracks are usually perpendicular to the surface of the cathode, forming islands of cathode on the interlayer. The size of cathode islands (spacing between microcracks) is typically between 100-200 microns. However, in some circumstances these microcracks can be significantly sharper and sometimes be within tens of microns.

[0007a] In one illustrative embodiment, an apparatus includes a cathode for use in a solid oxide fuel cell including a cathode layer possessing thermal expansion mismatch with an interlayer. The cathode layer contains microcracks forming cathode islands. The apparatus further includes a metallization layer covering more than 90 percent of the cathode.

[0008] Various advantages and novel features of illustrative embodiments are described herein and will become further readily apparent to those skilled in this art from the following detailed description. In the preceding and following descriptions, only the preferred embodiment of the invention has been shown and described, by way of illustration of the best mode contemplated for carrying out the invention. As will be realized, the described embodiment is capable of modification in various respects without departing from the scope of the invention as defined by the accompanying claims. Accordingly, the embodiments described herein and depicted in the drawings are to be regarded as illustrative in nature, and not as limiting the scope of the invention as defined by the claims.

Description of the Drawings

[0009] Figure 1 shows the typical cell configuration of anode-supported LSCF-based SOFCs.

[0010] Figure 2 shows a comparison of electrochemical performance with different metallization layers.

[0011] Figure 3 shows the effects of cathode thickness on the stability of the LSCF cells with fully covered metallization.

[0012] Figure 4 shows the effect of firing temperature of the cathode layer.

[0013] Figure 5 shows the effect of varying the amount of pore former in the paste and the increasing the stability of fully covered LSCF cells.

[0014] Figure 6 shows the long term performance of a fully covered LSCF cell.

[0015] Figures 7a and 7b show micrographs of (a) a degraded cell and (b) a stable cell.

Description of the Preferred Embodiment

[0016] The following description includes the preferred best mode of one embodiment of the present invention. It will be clear from this description that the invention is not limited to these illustrated embodiments but may also include a a variety of modifications thereto. Therefore the embodiments described herein should be seen as illustrative and not as limiting the invention as defined by the claims.

[0017] The following description provides information related to one proposed cell configuration and preparation conditions for the stable LSCF cells. While this example is set forth, it is to be distinctly understood that the invention is not limited thereto, but maybe variously alternatively configured according to the needs and necessities of the user.

[0018] Referring now to Figures 1-7, a variety of views of an illustrative embodiment of the present invention and various performance characteristics thereof are shown. Referring first now to Fig. 1. Fig. 1 shows the cell configuration of an anode-supported LSCF-based SOFC 10. This SOFC fuel cell 10 contains an anode 12, in this embodiment a Ni-YSZ anode, an electrolyte layer 14, an interlayer 16, a cathode 18, and a metallization layer 20 all stacked together. The interlayer 16 placed between the cathode 18 and the electrolyte prevents any reactions between them.

[0019] Cathode 18 is usually screen-printed on top of interlayer using a cathode paste that may or may not contain pore formers. After firing the cathode layer, the metallization layer (usually grid form) is also screen-printed on the cathode and then fired. This metallization layer is connected to the interconnects in order to supply the electrons to the cathode.

[0020] In this embodiment of the invention, the metallization layer 20 provides greater than 90 percent coverage over the cathode 18 and has a thickness ranging between 2~20 μm on an LCSF cathode 18 having a thickness generally between 2 ~ 80 μm. Preferably the metallization layer is made from a noble metal material such as Ag, however other metals, and other materials such as various ceramics may also be utilized in accordance to the specific needs and necessities of the user. The cathode is formed utilizing a firing temperature between 950 ~ 1100 °C and connected with a paste having a pore former having 0~30 vol% with respect to the volume of LSCF in the cathode forming paste.

[0021] Figure 2 shows a comparison of the electrochemical performance of the LSCF cells with different metallization layers. This figure shows that the stability of LSCF cells was greatly improved by using a fully covered metallization layer described above as compared to a cell with a grid. Figure 3 shows the effects of cathode thickness on the stability of the LSCF cells with fully covered metallization. The thicker cathode revealed more stable performance, although the initial power decreased with thickness of the cathode. Other factors such as firing temperature of cathode layer (Figure 4) and amount of pore former in the paste (Figure 5) also influenced the stability of fully covered LSCF cells. Figure 6 shows the long term performance of a fully covered LSCF cell, made according to the parameters set forth above. This cell revealed no degradation in power up to 2000 hrs of constant operation.

[0022] The degradation rate of the LSCF cathode has been determined to be closely related to the cell configuration and metallization as well as firing conditions, which influences the electrical conductivity and oxygen supply to the cathode. This embodiment optimized these variables to achieve stable performance of LSCF cathodes over 2000 hrs. Figure 7 shows the SEM micrographs of typical microstructures of a degraded cell and a stable cell (refer to (a) and (b), respectively). The stable cell contains microcracks in a cathode layer with 100-200 μm spacing. These microcracks help to relieve the stress caused by the thermal expansion mismatch between a SDC interlayer and a LSCF cathode layer and improve the oxygen diffusion to the cathode. Various modifications to the cathode thickness, the cathode firing temperature, the use of pore former influence the development of this microstructure.

[0023] This configuration enables us to use the cathode for SOFC applications that require a long operating time without experiencing performance degradation, such as auxiliary power supplies for automotive and residential power sources. While various preferred embodiments of the invention are shown and described, it is to be distinctly understood that this invention is not limited to the described embodiments but may be embodied in other ways that fall within the scope of the invention as defined by the following claims.

THE SUBJECT-MATTER OF THE INVENTION FOR WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED IS DEFINED AS FOLLOWS:

1. An apparatus comprising:

a cathode for use in a solid oxide fuel cell comprising a cathode layer possessing thermal expansion mismatch with an interlayer, wherein the cathode layer contains microcracks forming cathode islands; and

a metallization layer covering more than 90 percent of said cathode.

2. The apparatus of claim 1 wherein the cathode layer comprises lanthanum strontium cobalt iron oxide.

3. The apparatus of claim 2 wherein said cathode has a porosity of between 0 and 30 volume percent.

4. The apparatus of claim 2 wherein said metallization layer comprises at least one material selected from the group consisting of noble metals and alloys thereof.

5. The apparatus of claim 4 wherein said noble metal is Ag.

6. The apparatus of claim 4 wherein said alloys are Ag alloys.

7. The apparatus of claim 6 wherein said alloy is a Ag:Pd alloy.

8. The apparatus of claim 2 wherein said cathode has a thickness ranging from 2 μm to 80 μm.

9. The apparatus of claim 2 wherein said metallization layer has a thickness of between 10 and 25 percent of the thickness of the cathode.

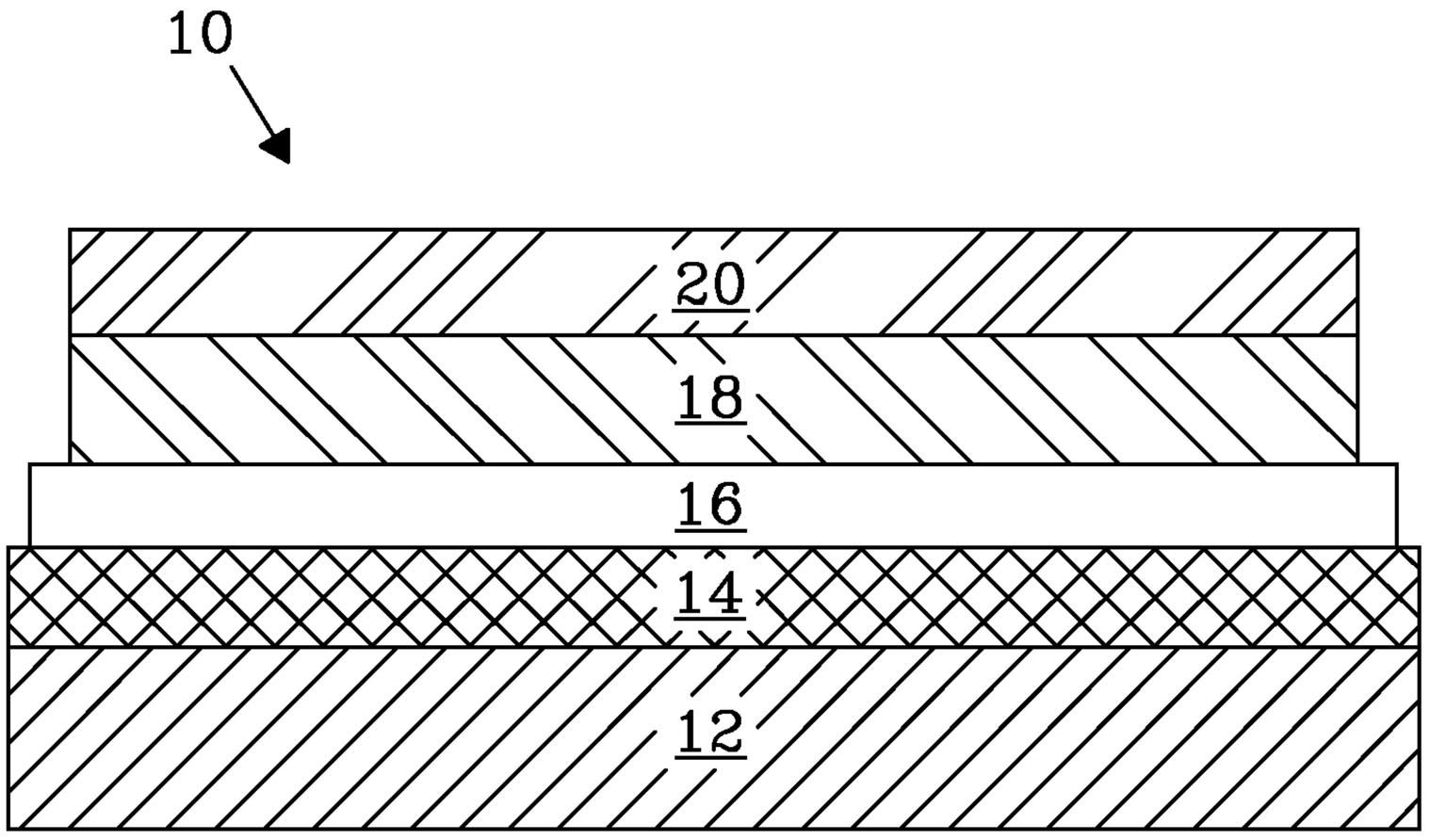
10. The apparatus of claim 2 wherein said cathode is formed by heating of a paste at a temperature between 950°C and 1100°C.

11. The apparatus of claim 10 wherein the paste has a pore former volume of between 0 and 30 vol % with respect to the volume of lanthanum strontium cobalt iron oxide in the cathode forming paste.

12. The apparatus of claim 2 wherein the microcracks have 100 μm to 200 μm spacing.

13. The apparatus of claim 2 wherein modification of fabrication parameters including thickness, firing temperature, and pore former allows formation of the microcracks.

14. The apparatus of claim 2 wherein use of patterned screens or deposition of disconnected islands of cathode materials allows simulation of a microstructure of the microcracks.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20
18
16
14
12

Fig. 1

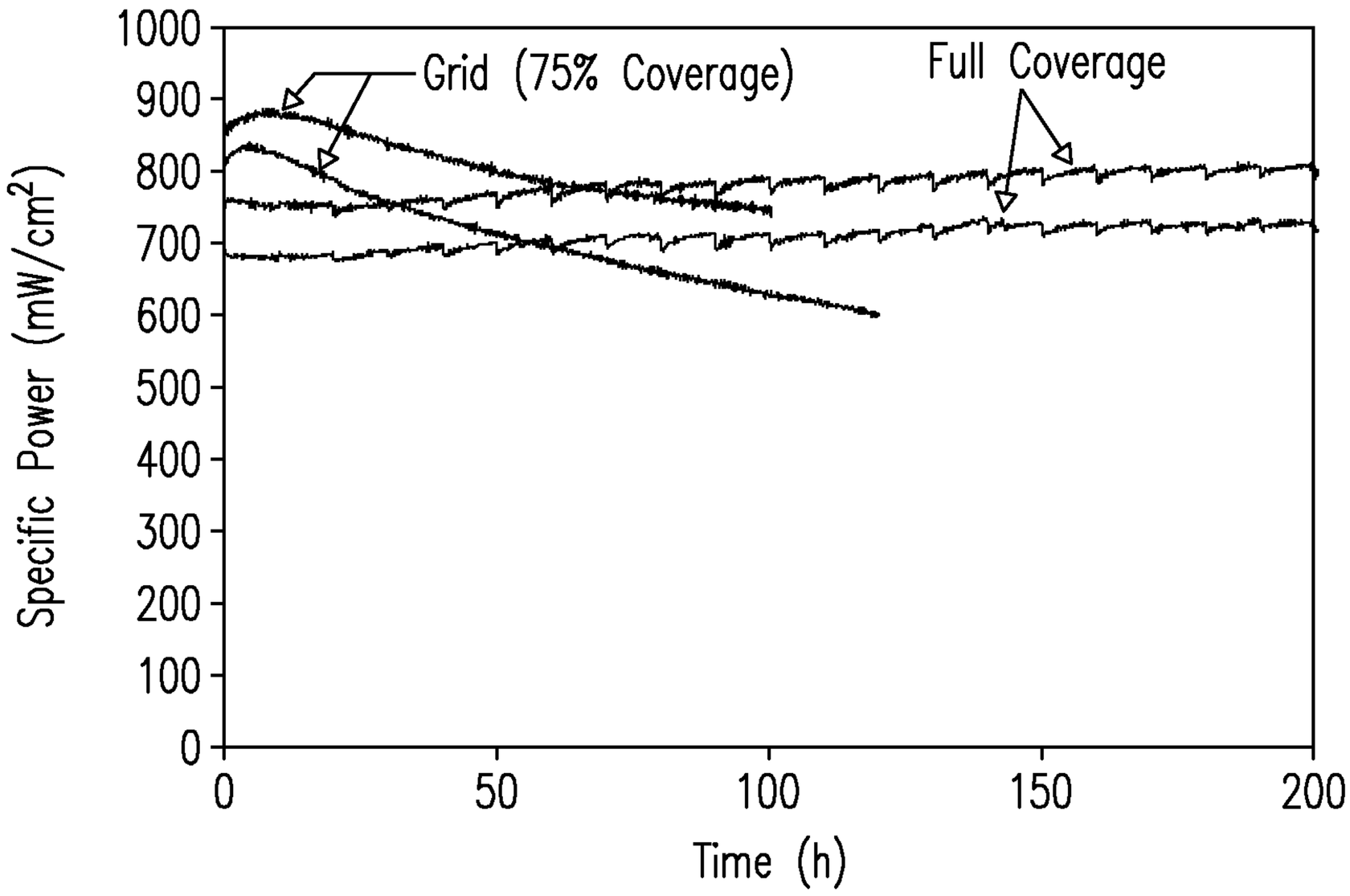
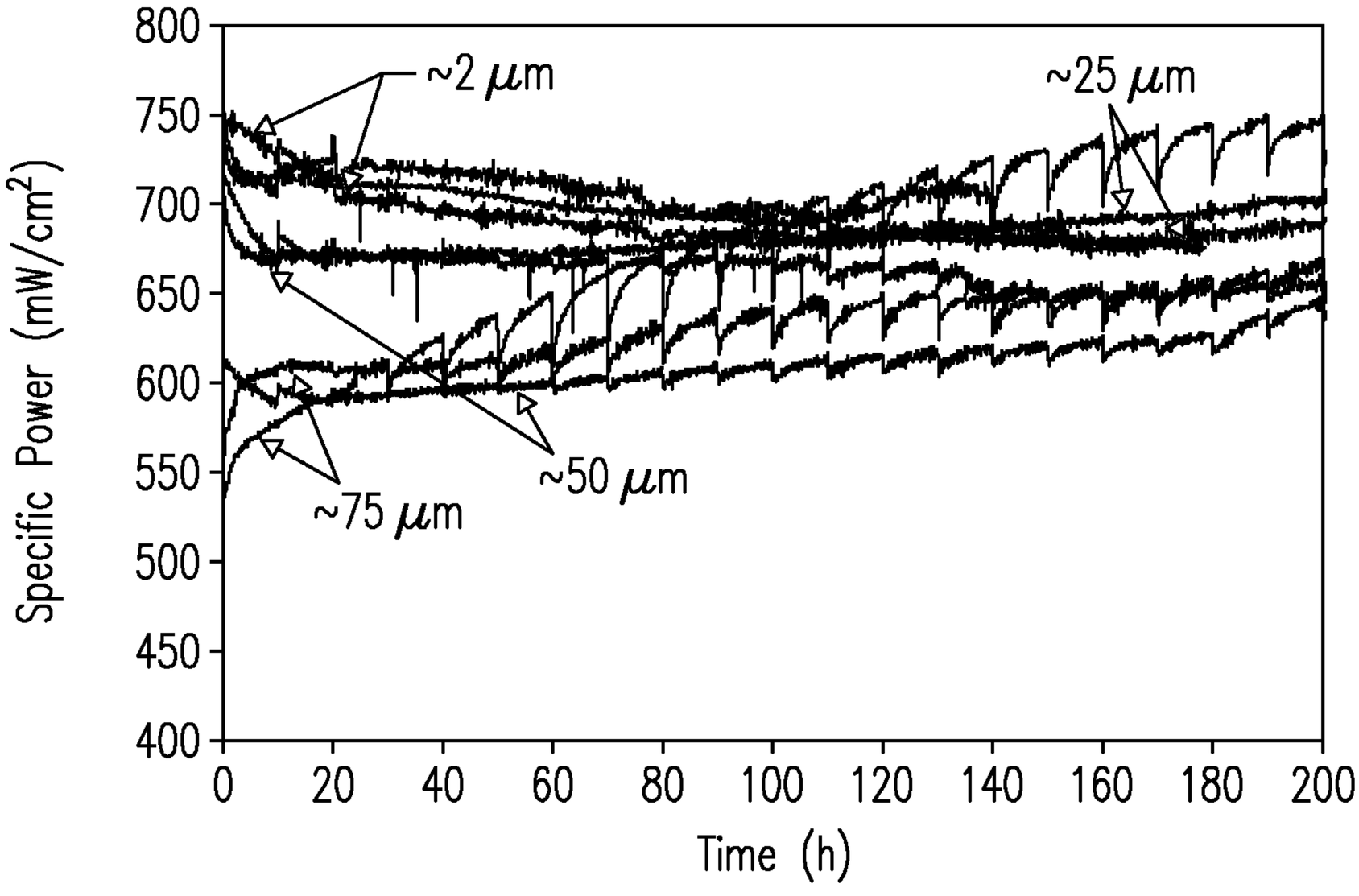

Grid (75% Coverage)
Full Coverage
Specific Power (mW/cm²)
1000
900
800
700
600
500
400
300
200
100
0
0
50
100
150
200
Time (h)

Fig. 2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650
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400
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20
40
60
80
100
120
140
160
180
200
Specific Power (mW/cm2)
Time (h)
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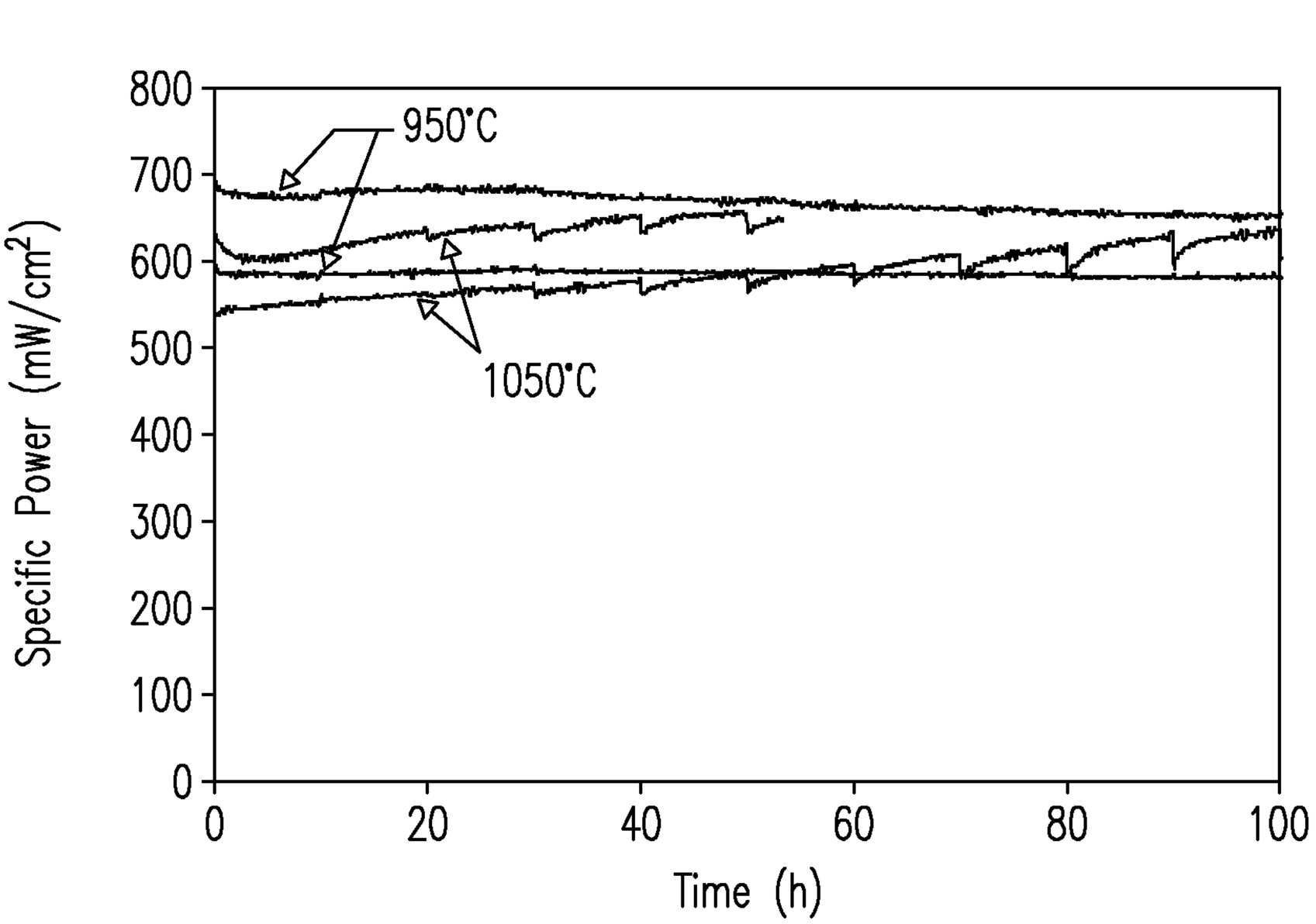
~25 μm
~50 μm
~75 μm

Fig. 3


800
700
600
500
400
300
200
100
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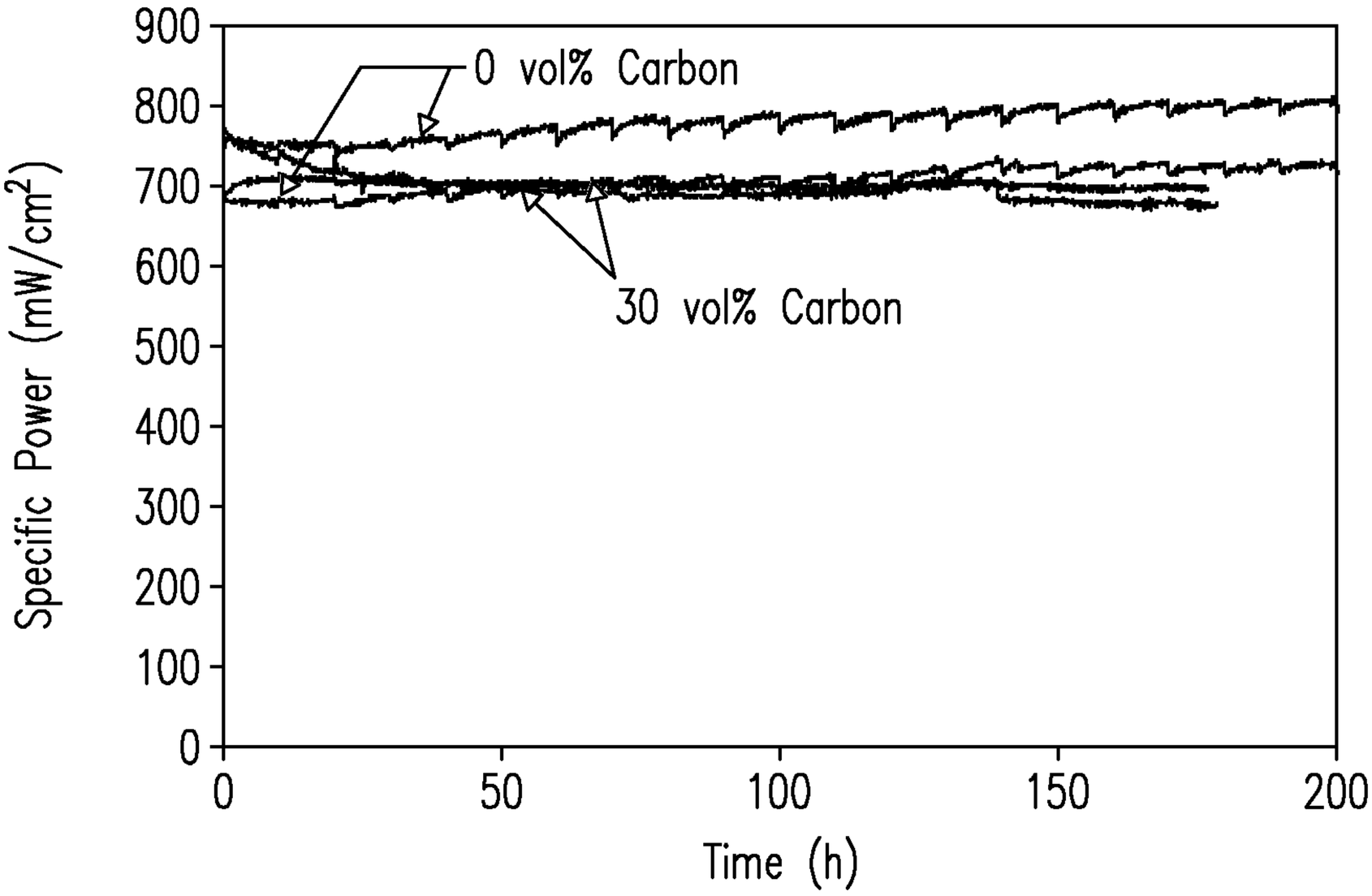
20
40
60
80
100
Specific Power (mW/cm2)
Time (h)
950°C
1050°C

Fig. 4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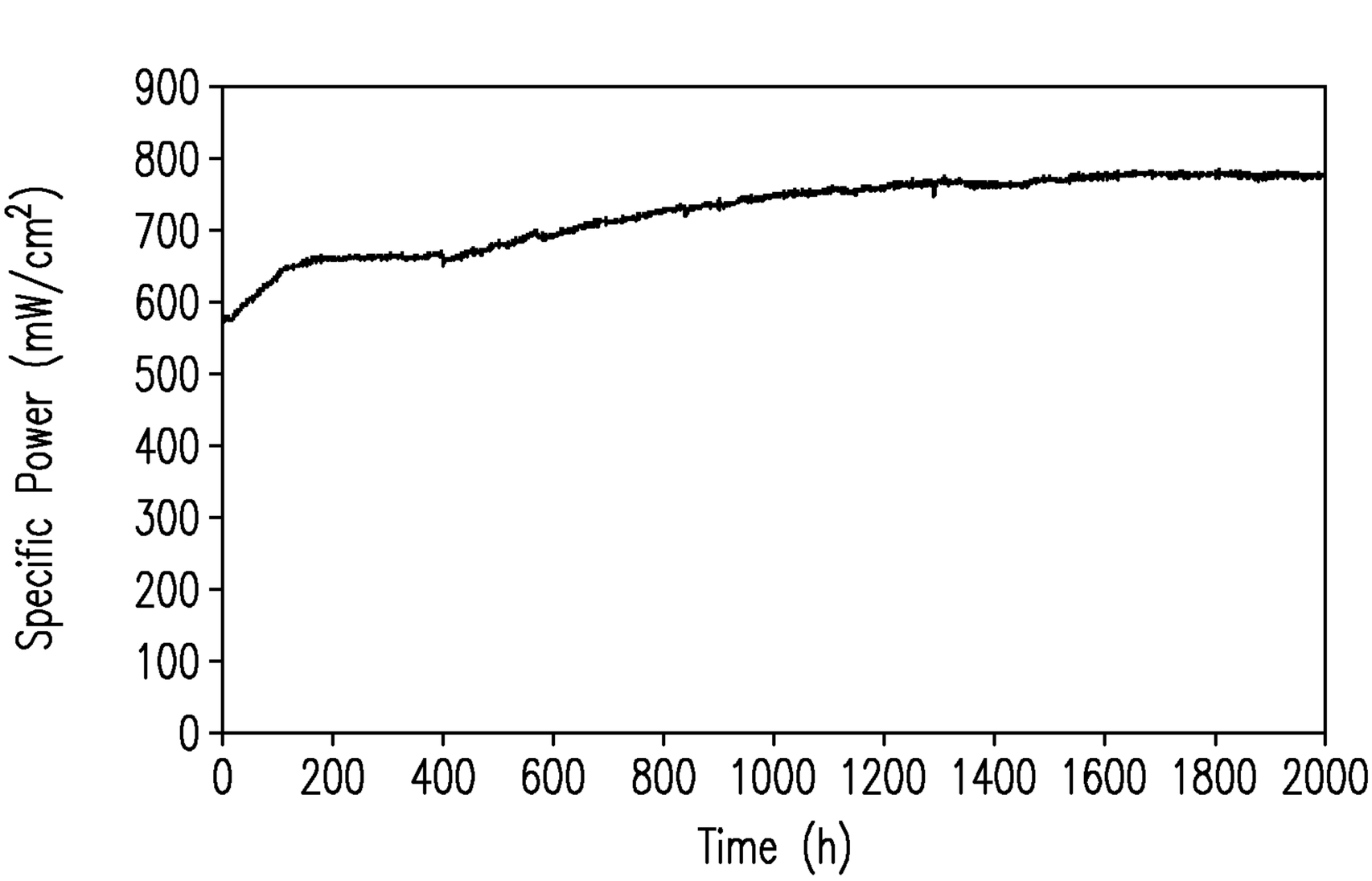
Time (h)

Fig. 5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700
600
500
400
300
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400
600
800
1000
1200
1400
1600
1800
2000
Time (h)

Fig. 6

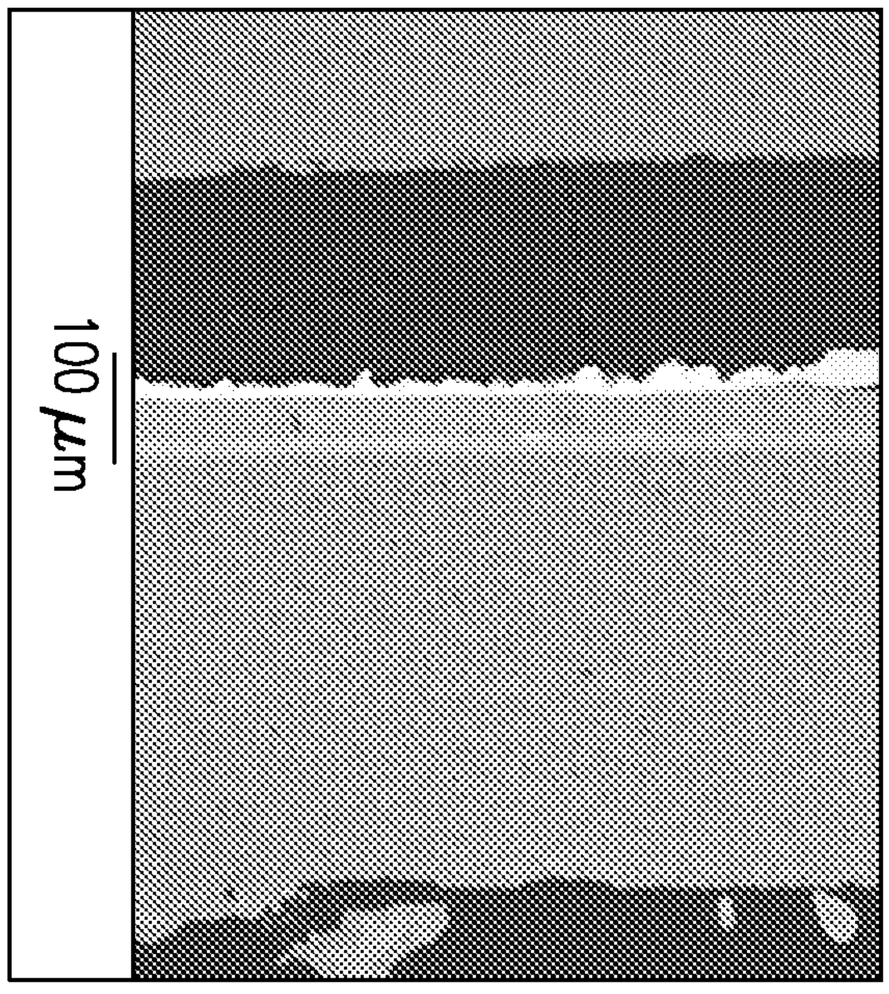


Fig. 7a

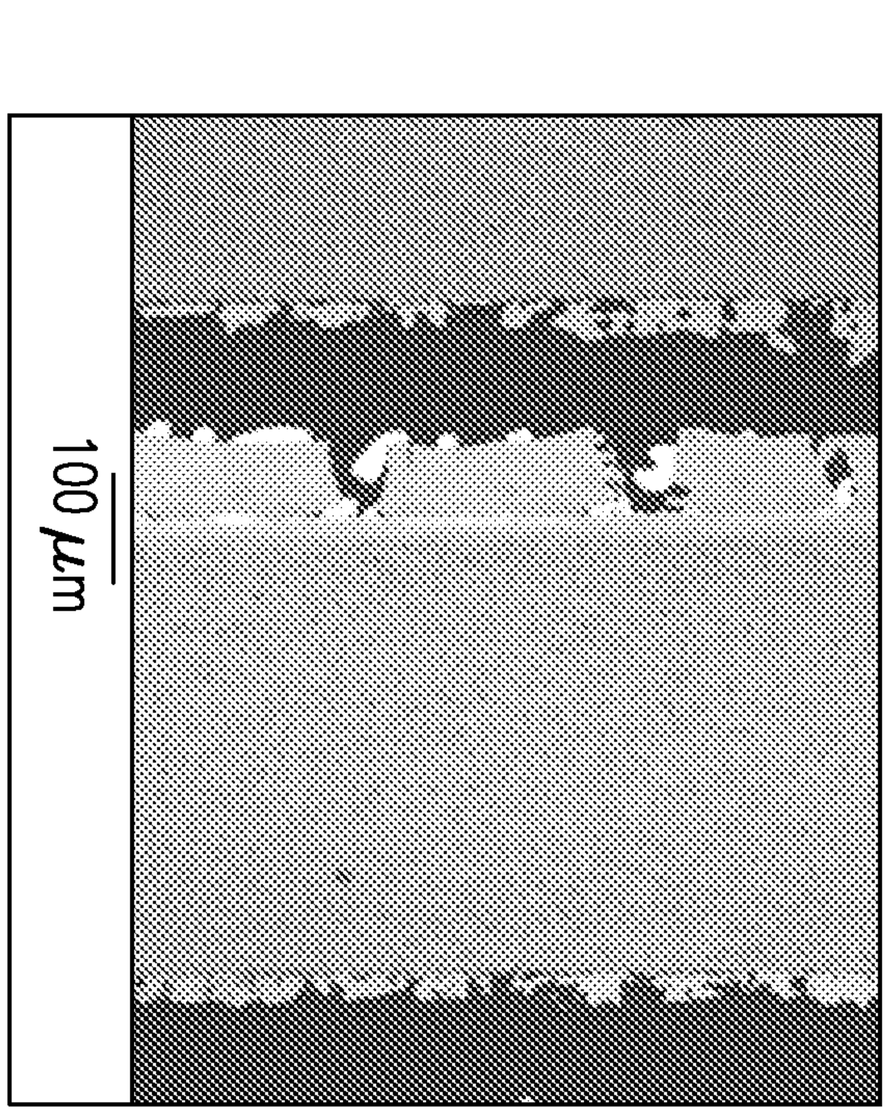
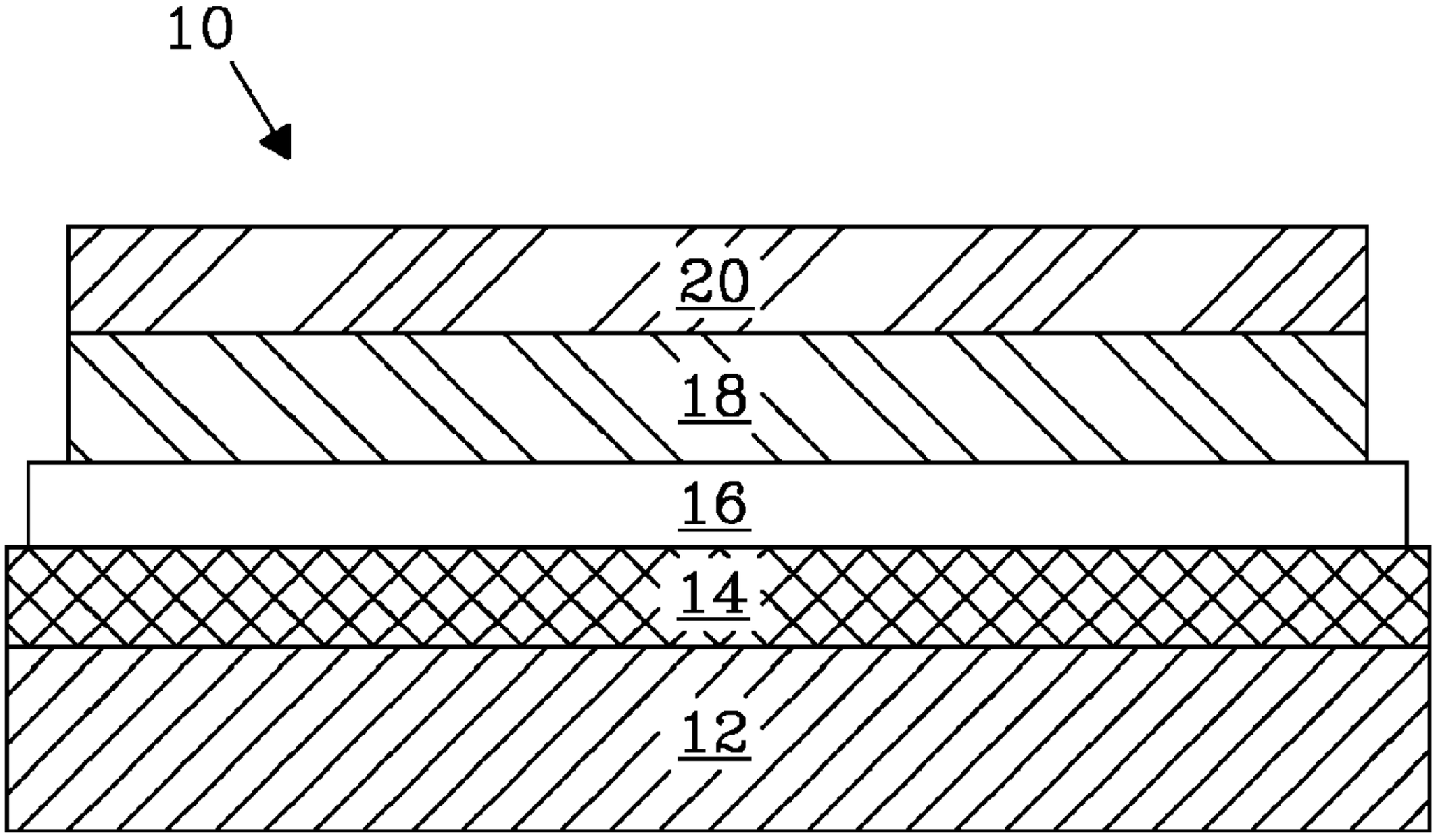


Fig. 7b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